CCCLXXIII.—*The Photochemical Decomposition of Glyoxal.*

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GLYOXAL in its monomeric form is a volatile yellow liquid (b. p. 50°) and constitutes the simplest of organic coloured compounds. It has been found possible to keep the dry gas in a tube for several hours without rapid polymerisation. Its photochemistry does not appear to have been studied, although its absorption spectrum in the gaseous state has been measured by Purvis and McCleland (J., 1912, **101**, 1810) and by Luthy (*Z. physikal. Chem.*, 1923, **107**, 302). The last author found a very large number of narrow absorption bands stretching from the blue at 4548 Å.U. to the ultra-violet at *ca.* 3000 Å.U., but measurement of fine structure became difficult after λ 3400 Å.U. on account of the weakness of absorption. The results of Purvis and McCleland are in general agreement with these observations. The strongest absorption occurs in the blue-violet region for a group of bands lying between 4554 and 4123 Å.U., those lying beyond this region being much weaker and only measurable at higher pressures.

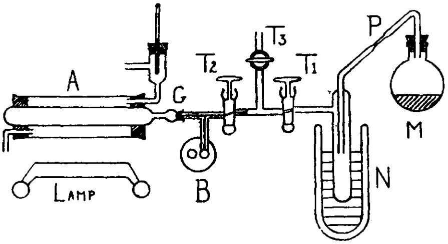
It was therefore considered of interest to investigate the photochemistry of glyoxal vapour, especially as the results might eventually be expected to be of importance biochemically, as, for instance, in connexion with the problem of photosynthesis.

EXPERIMENTAL.

(A) *The Photochemical Decomposition.*

The photochemical experiments were carried out in the all-glass apparatus shown in Fig. 1. The monomeric glyoxal was prepared as required by heating a mixture of solid (polymeric) glyoxal and phosphoric oxide in the bulb *M*, after the method of Harries and Temme (*Ber.*, 1907, **40**, 165). The reaction gives rise to a mixture of carbon monoxide, carbon dioxide, and glyoxal vapour, and the last two were separated from the first by condensation in the liquid-air trap, *N*. When sufficient glyoxal had been prepared, the preparation bulb was sealed off at *P*, and the carbon monoxide pumped away from the trap by a Toepler pump *via* tap T_3. The trap was next surrounded by a freezing mixture of ice and hydrochloric acid at — 25°, a temperature at which practically all the glyoxal was retained whilst the carbon dioxide could be pumped away. The glyoxal was stored in the trap surrounded by liquid air, and could be kept thus for at least a day without much polymerisation.

FIG. 1.



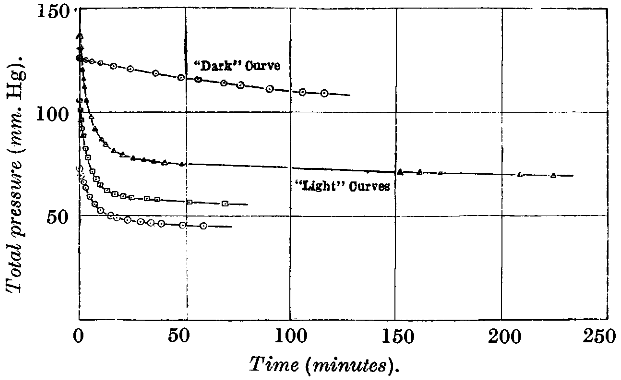
The reaction chamber consisted of a glass, water-jacketed vessel, *A*, of 75 c.c. capacity, connected with the rest of the apparatus by the ground-glass joint, *G*, and kept at 25° by means of water pumped from an electrically regulated thermostat.

After complete evacuation of the apparatus, the glyoxal in the trap was allowed to attain room temperature, and the reaction chamber was filled to the desired pressure *via* taps T_1 and T_2, pressures being measured on the mercury manometer, *B*. The vapour was then exposed to the action of light, and readings of the manometer were taken at short intervals of time.

In a preliminary experiment the unfiltered light from a 1000-c. p. filament lamp was used. The pressure in the reaction vessel decreased rapidly at first, and this rate of decrease diminished progressively with time.

The unfiltered light from a 3000-c. p. mercury-vapour lamp was used in all subsequent experiments, and in view of the fact that glass apparatus was employed, the light from the lamp in the regions 436, 405, and 365 $\mu\mu$ actually reached and was partly absorbed by the glyoxal. With this lamp the rate of decrease of pressure was greater than with the filament lamp, and the change was nearly complete in 20 mins., but, although the pressure tended asymptotically to approximately half the initial value, even after 4 hours' illumination it did not quite reach this value. The filament lamp gave similar results. Typical curves are shown in Fig. 2.

Fig. 2.



The fall of pressure in the first half-minute was always less than in the succeeding half-minute, a fact which is probably due to a slight heating (Draper) effect owing to the onset of photochemical reaction in the vapour.

Over the major part of their courses the curves approximately conform to a bimolecular law with respect to the decomposing glyoxal. Table I shows some typical experiments at 25°, P_t being the observed pressure (in mm.) after t mins. of illumination, and k being the bimolecular velocity coefficient calculated from the equation $k = 1/P_0t. [(P_0 - P_t)/(P_t - \frac{1}{2}P_0)]$.

During the reaction the green colour of the glyoxal gradually faded and could not be detected after about 1 hour, while a glassy,

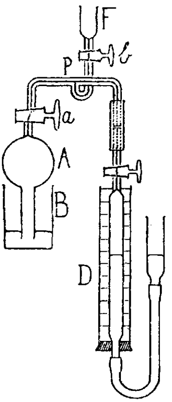
TABLE I.

t.	P_t.	$10^5 . k$.	P_t.	$10^5 . k$.	P_t.	$10^5 . k$.	P_t.	$10^5 . k$.	P_t.	$10^5 . k$.
0	53·5	—	72·5	—	105	—	126·2	—	132·7	—
2	50·5	118	66·3	145	93·9	126	111·0	127	116·5	122
4	47·5	140	61·5	152	84·6	150	101·2	130	105·7	129
6	44·7	155	57·4	165	79·0	155	94·8	131	97·7	140
8	43·0	155	54·8	166	74·9	159	89·2	140	92·5	145
10	41·5	154	52·8	165	72·3	157	85·8	141	89·1	144
12	40·2	155	51·5	159	70·4	153	83·4	139	86·2	147
15			50·0	151	68·2	148	81·0	133	83·3	146
20			48·7	133	66·0	137	78·4	124	80·8	135

white solid appeared chiefly on the lower surface of the reaction vessel.

The residual gas at the end of the reaction was pumped out and analysed as described below; subsequent illumination of the residual solid failed to produce any further gaseous products.

FIG. 3.



In view of the fact that glyoxal vapour polymerises slowly (Harries and Temme, *loc. cit.*; Harries, *Ber.*, 1913, **46**, 294), a blank run was carried out in which the vapour was not illuminated. The rate of decrease of pressure was small compared with that observed when the vapour was illuminated, as is seen from the "dark" curve shown in Fig. 2.

Analysis of Gaseous Products.—The analysis of three samples of gas collected at the ends of the several runs gave quite concordant results (Table II), and was carried out in an apparatus (Fig. 3) adapted from that used by Dr. M. Brunner (private communication), to whom we wish to express our thanks.

The bulb, *A*, could be filled with mercury from the beaker, *B*, by connecting the wide-mouthed tube, *F*, to a filter pump and opening taps *a* and *b*. The gas was passed from the burette, *D*, to the bulb, *A*, where it was subjected to the action of the requisite reagent, which had been previously introduced into *A* by a pipette with a bent jet. Water introduced from *F* was used for washing the gas before the volume was finally measured in *D*. The form of the bent T-piece, *P*, prevented any gas bubbles from collecting at this joint.

TABLE II.

Gas.	I.	II.	III.
CO	97·0%	97·0%	96·5%
H_2	2·7	2·5	2·5
Unsaturated compounds	0·3	0·4	0·9
Total	100·0	99·9	99·9

It appears from these results that under illumination from the mercury-vapour lamp, through glass, glyoxal decomposes in the main according to a bimolecular reaction, two volumes reacting to give one volume of carbon monoxide and a solid product. We may therefore write the empirical equation

$$2C_2H_2O_2 = CO + C_3H_4O_3 \quad . \quad . \quad . \quad . \quad (1)$$

The fact that hydrogen is also found to a small extent in the decomposition products suggests the reaction

$$C_2H_2O_2 = H_2 + 2CO \quad . \quad . \quad . \quad . \quad (2)$$

and the relative quantities of carbon monoxide and hydrogen in Table II show that about 98·5% of the decomposition may be represented by reaction (1) and 1·5% by reaction (2). The occurrence of reaction (2) would further account for the fact that the exact ratio of 2 : 1 for the initial to final pressures was never quite reached.

Although these equations satisfactorily represent the observed course of the reaction, it seemed possible, as an alternative, that glyoxal might exist as an equilibrium mixture of whole and half molecules $C_2H_2O_2$ and ·CHO (compare N_2O_4 and NO_2), and if this equilibrium were largely in favour of dissociation the facts might be represented by the equation

$$2CHO = CO + CH_2O \longrightarrow [\text{polymerised product}] \quad . \quad (3)$$

This view was tested by a determination of the vapour density of glyoxal. By weighing a dry bulb of known volume first full of air, and then full of glyoxal vapour at a known temperature and pressure, the molecular weight was found to be 58·7, corresponding closely to the formula $C_2H_2O_2$ (Calc. : *M*, 58·0), and therefore renders inadmissible any explanation of the facts based on thermal dissociation of the glyoxal.

(B) *The Nature of the Solid Product.*

The white solid produced in the reaction vessel was difficult to separate, since it adhered strongly as a glassy skin to the surface. It was slowly but extremely soluble in water, and easily soluble in alcohol, producing uncrystallisable solutions. It was slightly soluble in ether and acetone and insoluble in benzene. On heating, it decomposed without melting at 200°. It was somewhat hygroscopic, and always acquired moisture during attempts to scrape it from the surface of the vessel. In the earlier work it was therefore extracted by absolute alcohol, the solvent being subsequently removed as completely as possible by distillation first under reduced pressure at 30° and finally at 60° under a high vacuum.

It was found, however, that the weight of solid extracted in this way was always somewhat greater than that to be expected from equation (1) and the known quantities of glyoxal reacting, and it seemed probable that some combination had occurred between the original solid and the alcohol, a conclusion which received further confirmation from the analytical data below. Moreover, the alcoholic extract was much more hygroscopic than the original white solid.

In later work, the white solid was removed from the reaction vessel by cutting the latter into sections and scraping vigorously with a sharp knife. The *substance* so obtained was then dried to a constant weight at 75°/1 × 10^{-4} mm., whereby it lost 3·1% of its weight during 2 days (Found, for dried material: C, 40·5; H, 4·3. $C_3H_4O_3$ requires C, 40·9; H, 4·6%).

The *substance* extracted by alcohol was analysed by three separate micro-estimations, two of which were kindly carried out for us by Professor Haworth, F.R.S. (Found: C, 42·8, 42·6, 42·4; H, 5·7, 5·6, 5·5. $C_{11}H_{18}O_{10}$ requires C, 42·6; H, 5·8%), and it therefore seems clear that the composition of the product is changed by reaction with alcohol during the process of extraction.

Molecular Weight.—The molecular weight of the solid in aqueous solution was determined by the Beckmann freezing-point method. On account of the small amount of material available it was necessary to work with solutions of about 0·05 g. of solid in 7 g. of water. Control experiments on similar quantities of purified glucose ($C_6H_{12}O_6,H_2O$) or sucrose and water constantly gave results for the molecular weights within 8% of the theoretical. Three series of determinations with the solid scraped from the reaction tube gave 332, 365, and 342 for the initial value of the molecular weight. This value decreased progressively with time until, in the latter two cases, final constant values of 90·8 ± 5 and 89·5 ± 5 were obtained. The following figures indicate the results of a typical experiment, the temperature being raised to 16° between each determination :

Wt. of solid, 0·0424 g.; wt. of water, 6·59 g.

Age of solution (mins.)	30	70	100	150	220	270	∞
Mean lowering of f. p.	0·035°	0·0525°	0·055°	0·0605°	0·069°	0·077°	0·134°
Molecular weight	342	288	218	198	173	155	89·5

Since the molecular weight of $C_3H_4O_3$ is 88, it appears that the polymeric substance deposited in the reaction vessel changes in solution to give the monomeric form. In view of the slow rate of solution, an hour being sometimes required at room temperature, it is not possible to make any certain deductions as to the molecular weight of the polymerised form, for considerable depolymerisation may have occurred before the initial readings are taken.

Further determinations were carried out on the alcoholic extract; two experiments gave mean values of 300 and 308, whence, in conjunction with the analytical data, we conclude $C_{11}H_{18}O_{10}$ or $(C_3H_4O_3)_3,C_2H_6O$ (Calc.: M, 310) to be the formula of the extracted solid. The molecular weight of this substance changed on standing, giving final values of 98 ± 5 and 102 ± 5, and attaining the final value more quickly if the solution was warmed to 35°. This figure is somewhat higher than that for the white solid itself, a result which suggests that the molecule of alcohol associated with the polymerised molecule remains attached to one of the depolymerised forms, so that the apparent molecular weight falls to one-third of its original value.

Pseudo-acidic Character of the White Solid.—In an aqueous solution of the solid scraped from the reaction vessel, a gradual development of acidity occurred, even when the solution was kept in an atmosphere of hydrogen. This slow change took place at the ordinary temperature over a period of weeks, and was later traced to the fact that the monomeric product exists in two forms, one of which is strongly acidic. The equilibrium mixture of the two exhibits the phenomenon of progressive neutralisation similar to that described by Kling (*Compt. rend.*, 1905, **140**, 1256) for hydroxyacetone, the slow development of acidity being due to the slowness of the change of the non-acidic to the acidic form. This change takes place much more rapidly at higher temperatures, and complete titration of the mixture can be effected in less than an hour at 100°. In these experiments, the most satisfactory end-point was obtained with litmus, although fairly satisfactory results were also obtained with phenolphthalein.

As an example, the following experiment may be recorded: A solution of 0·0258 g. of the white solid in 10 c.c. of water required 0·9 c.c. of $N/20$-sodium hydroxide for neutralisation (litmus). On continued boiling, the titre increased progressively to a final value of 5·15 c.c. in the course of 1 hour. These figures give an initial equivalent of 570 and a final equivalent of 100, but slight decomposition had occurred at the end of the experiment. Another experiment, with smaller quantities and $N/100$-alkali, gave an initial equivalent of 440 and a final value of 88, whilst a third experiment gave 650 and 86, respectively. The first and third experiments were made with fresh solutions; the second, however, was done with a solution which had stood for 13 days and in which equilibrium had probably become established. Therefore, if 440 and 88 be taken as the most probable initial and final equivalents, it would appear that at equilibrium about 20% of the dissolved substance is in the acid form.

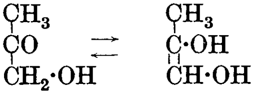
The equivalent of the acid form was further measured by heating the white solid under reflux on the water-bath with excess of sodium hydroxide for about 40 mins. Back titration with standard hydrochloric acid gave values of 94 ± 10 and 99 ± 10 for the equivalent. The results of these and the previous experiments are not quite accurate owing to the fact that the white solid is slightly decomposed by continued boiling, giving a brown solution, but the values obtained are in sufficiently close agreement with the theoretical value of 88 for $C_3H_4O_3$, and with the cryoscopic value of 90.

The evidence for the tautomerism of the monomeric substance in solution is further supported by an instantaneous reversible colour change which the solution undergoes on treatment with acids and alkalis. A drop of *N*-sodium hydroxide produces a bright yellow coloration which is immediately discharged on neutralisation by *N*-hydrochloric acid. This colour change can be repeated in the same specimen indefinitely. In addition, bromine water added to the aqueous solution drop by drop is at first instantly decolorised, whilst further quantities react slowly.

The sodium salt was prepared by dissolving together equivalent quantities of the white solid and sodium carbonate in the smallest possible quantity of water. The whole was kept at 60° for 6 hours, the colour of the solution turning gradually from lemon-yellow to dark red. A drop of this red solution on dilution gave a lemon-yellow solution, the colour of which was discharged by acidification with hydrochloric acid, and it was therefore concluded that the development of the red colour corresponded with the progressive neutralisation of the pseudo-acid and the gradual increase in concentration of its sodium salt. When the red solution was allowed to evaporate slowly in a desiccator over phosphoric oxide, it gradually became more viscous, and finally dried to a red, glassy substance without crystallising. This product was very hygroscopic, absorbing water from the air to form a red, treacly mass. In dilute solution it was yellow, the colour being discharged by acidification.

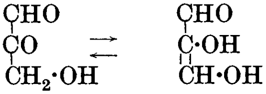
Reducing Properties of the White Solid.—The aqueous solution, in addition to its action with bromine water, showed other strong reducing actions. It apparently converted ferric into ferrous chloride, and reduced Benedict's and Fehling's solutions in the cold, thus differing from glyoxal, which does not react with Fehling's solution. These reactions indicate the existence of an aldehyde group in the molecule, and this conclusion was confirmed by the observation that the solution readily reacts with phenylhydrazine (see below). The aldehyde group was estimated by the method of Cumming, Hopper, and Wheeler (" Systematic Organic Chemistry," 1923, 479) : an excess of standard potassium bisulphite was added to a known quantity of the aqueous solution of the " alcoholic extract," and the excess titrated with iodine. Two separate determinations gave equivalents of 102 and 96 referred to one aldehyde group, in good agreement with the theoretical value $\frac{1}{3} \times 310 = 103$ for the depolymerised form of the alcoholic extract.

These results are satisfactorily explained if, by analogy with Kling's formulæ for hydroxyacetone, (I) and (II), we adopt the



$$\begin{array}{c}CH_3\\ |\\ CO\\ |\\ CH_2{\cdot}OH\end{array} \rightleftharpoons \begin{array}{c}CH_3\\ |\\ C{\cdot}OH\\ \|\\ CH{\cdot}OH\end{array}$$

(I; neutral.) (II; acid.)



$$\begin{array}{c}CHO\\ |\\ CO\\ |\\ CH_2{\cdot}OH\end{array} \rightleftharpoons \begin{array}{c}CHO\\ |\\ C{\cdot}OH\\ \|\\ CH{\cdot}OH\end{array}$$

(III; neutral.) (IV; acid.)

formulæ (III) and (IV) as representing the desmotropic forms of the monomeric glyoxal product. The source of the acidity is to be sought in the hydroxymethylene group, of which the tendency to develop strongly acidic properties when in combination with two electronegative groups is well known. For example, hydroxyacetone, hydroxymethylenecamphor, acetylacetone, acetoacetic and malonic esters all approach, and in some cases surpass, the monocarboxylic acids in strength, and may be represented as derivatives of formic acid by the general structure $CXX'{:}CH{\cdot}OH$ (Claisen, *Annalen*, 1897, **297**, 1; *Ber.*, 1893, **26**, 2731). Just as in the case of hydroxyacetone, however, so in the present instance, the change of the neutral into the acid form is slow, so that complete neutralisation by alkali only takes place gradually.

The micro-preparation of the following derivatives confirms the structure assigned to the decomposition product.

Quinoxaline Derivative.—0·04 G. of the white solid was dissolved in 1 c.c. of water, kept at 40° until depolymerised, mixed with 0·05 g. of recrystallised *o*-phenylenediamine dissolved in 1 c.c. of water, and the whole warmed to 60°. The yellow precipitate which formed rapidly was recrystallised from aqueous alcohol, and then had m. p. 165° (Found, by microanalysis : N, 15·3. $C_9H_8ON_2,H_2O$ requires N, 15·7%); it was somewhat soluble in both hot and cold water, and dissolved easily in dilute hydrochloric acid to give a brown solution from which it was reprecipitated by soda. This condensation may be taken as proof of the juxtaposition of two carbonyl groups in the molecule.

Reaction with Phenylhydrazine.—The aqueous solution of the white solid when added to a solution of redistilled phenylhydrazine in 50% acetic acid gave *in the cold* a bright yellow precipitate which, when separated and recrystallised from aqueous alcohol, had m. p. 161° (Found, by microanalysis : C, 70·3 ; H, 5·9 ; N, 23·0. Calc. for $C_{21}H_{20}N_6$: C, 70·8 ; H, 5·6 ; N, 23·6%). If the reaction was carried out on a water-bath, the yellow precipitate first obtained rapidly turned brownish-red, and after recrystallisation from aqueous alcohol melted at 132° (Found : C, 70·2 ; H, 5·8 ; N, 23·0%). It would appear that these two products have the same composition.

The triphenylhydrazone of mesoxalic dialdehyde,

$$NHPh{\cdot}N{:}C(CH{:}N{\cdot}NHPh)_2,$$

has been obtained by von Pechmann (*Ber.*, 1891, **24**, 3257) as a yellow substance, m. p. 166°, and by Harries and Türk (*Ber.*, 1905, **38**, 1636) as a brown substance, m. p. 156° ; but in view of the method of preparation used by von Pechmann, it seems that his compound is better represented by the isomeric azo-formula $NHPh{\cdot}N{:}C(CH_2{\cdot}N{:}NPh)_2$. It is therefore probable that our condensation products consist largely of these two isomeric substances.

As has already been seen, however, the white solid in solution gives an equilibrium mixture of two isomeric substances, and the possibility of the formation of the monophenylhydrazone of the *aci*-form, which is present to the extent of about 20%, must not be overlooked. The product of reaction with phenylhydrazine would thus contain a small quantity of the substance

$$NHPh{\cdot}N{:}CH{\cdot}C(OH){:}CH{\cdot}OH ;$$

indeed, an admixture of 7% of this compound with the triphenylhydrazone would have the composition C, 70·1 ; H, 5·6 ; N, 23·0%, which is in close agreement with the analytical figures given above. A partial confirmation of this view was obtained by the observation that a small portion of both the yellow and the red product could be extracted by cold sodium hydroxide to give a yellow solution. Acidification turned this solution cloudy and discharged its colour, which was regenerated by the addition of alkali. Continued action of caustic soda on the original phenylhydrazine derivatives did not extract any further material, so it appears probable that it is the monophenylhydrazone of the enolic form which is thus extracted

The reaction with phenylhydrazine is in agreement with the formulæ proposed for the white solid if we assume that the predominant (non-acidic) form of the latter is capable of undergoing an " osazone " oxidation to form the triphenylhydrazone in the cold, and that at the same time the *aci*-form reacts to form a monophenylhydrazide in smaller quantity. This result is consistent with the fact that the rate of change of the one form of the white solid into the other is very slow.

Reaction with Hydroxylamine.—0·093 G. of the white solid, dissolved in 0·5 c.c. of water, was mixed with 0·16 g. of hydroxylamine hydrochloride dissolved in 0·5 c.c. of water and warmed; the mixture turned brown. 0·12 G. of sodium carbonate in 1 c.c. of water was then added, and after the effervescence had subsided the solution was warmed and allowed to stand for 24 hours. Two extractions of the clear brown solution with ether then yielded 0·053 g. of a white solid, m. p. 168° (decomp.) after drying under a high vacuum. It was soluble with difficulty in water and dilute hydrochloric acid, but easily soluble in soda. Its aqueous solution produced a dark red colour on warming with dilute cobalt acetate in the presence of sodium acetate, and sodium hydroxide then precipitated a green base, which redissolved to a dark red solution on acidification with hydrochloric acid. In all these respects the product acted like a glyoxime and it is believed that its structure corresponds to hydroxymethylglyoxime, $CH_2(OH){\cdot}C({:}N{\cdot}OH){\cdot}CH{:}N{\cdot}OH$.

(C) *The Kinetics of the Change.*

The absorption spectrum of glyoxal in the blue, violet, and near ultra-violet shows fine structure (see p. 2830), and in accordance with spectroscopic theory we must conclude that no spontaneous dissociation of the molecule takes place as the result of light absorption. The alternative, that a molecule of photo-activated glyoxal reacts with an inactive molecule, is therefore to be preferred, and the bimolecular nature of the reaction shows it to be conditioned by the probability of collision between active and inactive molecules. Thus, if g and g' represent the concentrations of inactive and active glyoxal molecules respectively, we have, at equilibrium

$$dg'/dt = k_1Ig - k_2gg' - k_3g' = 0,$$

where k_1 refers to activation, k_2 to reaction, and k_3 to deactivation of glyoxal molecules, and I represents the intensity of illumination. Hence $g' = k_1Ig/(k_2g + k_3)$, and the rate of reaction of glyoxal is therefore

$$- dg/dt = k_2gg' = k_1k_2Ig^2/(k_2g + k_3)$$

whence, if k_3 is large compared with k_2, the measurable reaction will be approximately bimolecular.

The final elucidation of the mechanism must await a further investigation of the quantum kinetics of this reaction, which is now being carried out.

Summary.

Glyoxal gas decomposes in the light of the mercury vapour lamp, probably through the agency of the blue, violet, and ultra-violet light at 3650 Å.U. The main reaction involves a bimolecular change, two volumes of glyoxal giving one volume of carbon monoxide and a polymerised solid product:

$$2C_2H_2O_2 = CO + (C_3H_4O_3) \longrightarrow \text{[polymerised product]}.$$

A second reaction to the extent of about 1·5% of the total change probably occurs with the production of hydrogen:

$$2C_2H_2O_2 = 2CO + H_2.$$

The solid product and its derivatives have been investigated, and its chemical properties, composition, and molecular weight are in accord with its representation as a polymeride of the hitherto unknown glycerosone to which it is hydrolysed in aqueous and acid solution.

The properties of glycerosone further suggest that in aqueous solution it exists in tautomeric equilibrium with an acidic hydroxymethylene form (III and IV), in analogy with other substances of this type.

The kinetics of the photochemical reaction is discussed.

We desire to express our thanks to Sir Robert Robertson, F.R.S., for granting facilities to one of us (J. G. A. G.) for continuing the cryoscopic experiments at the Government Laboratory. Our thanks are also due to the Governing Body of Emmanuel College, Cambridge, for assistance towards the maintenance of one of us (J. G. A. G.) while the work was in progress.

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